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(54)【発明の名称】 二次電池

(57)【特許請求の範囲】

1. 構成要素として少なくとも正極、負極、セパレータ一、非水電解液からなり、3.9V以上の起電力を有する二次電池であって、正極として、 LiCoO_2 及び/又は LiNiO_2 を用い、負極としてカーボン(BET法比表面積 A (m^2/g)が $0.1 < A < 100$ の範囲で、かつX線回折における結晶厚み L_c (\AA)と真密度 ρ (g/cm^3)の値が条件 $1.80 < \rho < 2.18$ 、 $15 < L_c$ かつ $120 \rho - 227 < L_c < 120 \rho - 189$ を満たす範囲にある炭素質材料を除く。)を用いることを特徴とする二次電池。

【発明の詳細な説明】

【産業上の利用分野】

本発明は新規な二次電池、更には小型、軽量二次電池に関する。

【従来の技術】

近年、電子機器の小型化、軽量化は目覚ましく、それに伴い電源となる電池に対しても小型軽量化の要望が非常に大きい。一次電池の分野では既にリチウム電池等の小型軽量電池が実用化されているが、これらは一次電池であるが故に繰り返し使用できず、その用途分野は限られたものであった。一方、二次電池の分野では従来より鉛電池、ニッケルカドミ電池が用いられてきたが両者共、小型軽量化という点で大きな問題点を有している。かかる観点から、非水系二次電池が非常に注目されているが、未だ実用化に至っていない。その理由の一つは該二次電池に用いる電極活物質でサイクル性、自己放電特性等の実用物性を満足するものが見出されていない点にある。

一方、従来のニッケルカドミ電池、鉛電池などと本質的に異なる反応形式である層状化合物のインターカレ

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CLAIMS

(57) [Claim(s)]

It is Rechargeable Battery Which Consists of Positive Electrode, Negative Electrode, a Separator, and Nonaqueous Electrolyte at Least as a Component, and Has Electromotive Force beyond 3.9V. 1. As a Positive Electrode LiCoO_2 and/or LiNiO_2 are used and it is carbon (in $0.1 < A < 100$, the BET adsorption method specific surface area A (m^2/g)) as a negative electrode. and the value of the crystal thickness L_c in an X diffraction (A), and true density ρ (g/cm^3) -- conditions $1.80 < \rho < 2.18$, $15 < L_c$, and $120\rho - 227 < L_c < 120\rho - 189$ is removed. The rechargeable battery characterized by using.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[Industrial Application]

This invention relates to a new rechargeable battery and also small, and a lightweight rechargeable battery.

[Description of the Prior Art]

In recent years, the miniaturization of electronic equipment and lightweight-izing are remarkable, and its request of the formation of small lightweight is very large also to the cell which serves as a power source in connection with it. Although small lightweight cells, such as a lithium cell, were already put in practical use in the field of the primary cell, although these were primary cells therefore, they could not be used repeatedly, but the application field was restricted. On the other hand, in the field of the rechargeable battery, although the lead cell and the nickel-cadmium cell have been used conventionally, both have the big trouble in respect of the formation of small lightweight. Although the nonaqueous rechargeable battery has attracted attention very much from this viewpoint, it has not yet resulted in utilization. One of the reason of the is in the point that what is satisfied with the electrode active material used for this rechargeable battery of practical use physical properties, such as cycle nature and a self-discharge property, is not found out.

The electrode active material of the new group using the intercalation or doping phenomenon of the stratified compound which is a reaction format which is essentially different from the conventional nickel-cadmium cell, a lead cell, etc. on the other hand attracts attention.

The extremely excellent charge-and-discharge cycle nature is expected from this new electrode active material not causing a complicated chemical reaction in the electrochemical reaction in the charge and discharge. Especially, using carbon as an active material is proposed and it attracts attention.

On the other hand, metal cull scorch night compounds, such as TiS_2 and MoS_2 , etc. were conventionally considered as a positive-electrode ingredient. However, when these things combined with carbon, the engine performance to the extent that electromotive force was expected small was not found out.

[Problem(s) to be Solved by the Invention]

Like the above-mentioned, selection of positive active material was left behind as a very important technical problem in the rechargeable battery which used carbon as a negative-electrode active material.

[The means and operation] for solving a trouble

This invention solves the above-mentioned trouble, and it is made in order to offer the small lightweight rechargeable battery of the cell engine performance especially the high performance excellent in output characteristics, and a high energy consistency.

It is the rechargeable battery which consists of a positive electrode, a negative electrode, a separator, and nonaqueous electrolyte at least as a component according to this invention, and has the electromotive force beyond 3.9V. As a positive electrode LiCoO_2 and/or LiNiO_2 are used and it is carbon (in $0.1 < A < 100$, the BET adsorption method specific surface area A (m^2/g)) as a negative electrode. and the value of the crystal thickness L_c in an X diffraction (\AA), and true density ρ (g/cm^3) -- conditions $1.80 < \rho < 2.18$, $15 < L_c$, and $120\rho - 227 < L_c$ -- the carbonaceous ingredient in the range which fills $L_c < 120\rho - 189$ is removed. The rechargeable battery characterized by using is offered.

Although not limited, if the example is given especially with the carbon as used in the field of this invention High surface area carbon materials, such as activated carbon given in JP,58-35,881,A, JP,59-173,979,A, JP,59-207,568,A, etc., Or baking carbide, such as phenol system resin given in JP,58-209,864,A etc., Moreover, a condensation polycyclic hydrocarbon given in JP,61-111,907,A, The carbon whisker obtained by carbonization of a heterocycle polycyclic compound, the vapor growth carbon fiber of a Japanese Patent Application No. [according to this invention persons further / No. 103,785 / 61 to] publication, Pitch system carbide (however, the BET adsorption method specific surface area A (m^2/g) in $0.1 < A < 100$) etc. and the value of the crystal thickness L_c in an X diffraction (\AA), and true density ρ (g/cm^3) -- conditions $1.80 < \rho < 2.18$, $15 < L_c$, and $120\rho - 227 < L_c$ -- the carbonaceous ingredient in the range which fills $L_c < 120\rho - 189$ is removed. It is mentioned.

When the carbon applied like the above-mentioned was used as a negative electrode, selection of the positive electrode to be used is very important, and this invention persons found out that the cell engine performance which was extremely excellent with the combination of LiCoO_2 and/or LiNiO_2 , and carbon was obtained.

LiCoO_2 and LiNiO_2 which are used by this invention are manufactured by the baking reaction with lithium compounds, such as a lithium carbonate and lithium oxide, cobalt and/or the metal of nickel and an oxide, a hydroxide, a carbonate, or a nitrate.

The rechargeable battery with new forward [by this invention] and combination of a negative electrode is that electromotive force is very as high as 3.9V-4.2V as the 1st description.

therefore -- although a carbon negative electrode shows the potential change before and behind 1V with the discharge like the above-mentioned -- the rechargeable battery of this this invention -- setting -- a negative-electrode side -- 1V -- even if a near voltage drop occurs, the electrical potential difference of the range practical still enough is maintainable.

As the 2nd description, each of carbon, and LiCoO_2 and LiNiO_2 is very stable compounds, can perform cell assembly easily and become a big advantage industrially. As a source of Li required for charge and a discharge reaction, it has already contained in

LiCoO₂ and LiNiO₂, and when using other positive-electrode ingredients 2, for example, TiS, and V₆O₁₃ grade, it is not necessary to use [like] a metal lithium etc. as a source of Li as the 3rd description, at the time of cell assembly. This is a industrial very big advantage.

The electrode using the active material of said this invention as a basic component in the case of assembling the nonaqueous rechargeable battery of this invention and also a separator, and nonaqueous electrolyte are mentioned. Although are not limited especially as a separator, and textile fabrics, a nonwoven fabric, a glass cloth, the synthetic-resin fine porosity film, etc. are mentioned, when using a thin film and a large area electrode like the above-mentioned, the synthetic-resin fine porosity film indicated by JP,58-59072,A, especially the polyolefine system fine porosity film are desirable in respect of thickness, reinforcement, and membrane resistance.

Although not limited especially as an electrolyte of nonaqueous electrolyte, if an example is shown, LiClO₄, LiBF₄, LiAsF₆, CF₃SO₃Li, LiPF₆, LiI, LiAlCl₄, NaClO₄, NaBF₄ and NaI, 4 (n-Bu) N⁺ClO₄, 4 (n-Bu) N⁺BF₄, and KPF₆ grade will be mentioned.

Moreover, as an organic solvent of the electrolytic solution used, although ether, ketones, lactone, nitril, amines, amides, a sulfur compound, chlorinated hydrocarbons, ester, carbonate, a nitro compound, a phosphoric ester system compound, a sulfolane system compound, etc. can be used, for example, ether, ketones, nitril, chlorinated hydrocarbons, carbonate, and a sulfolane system compound are desirable also among these.

Furthermore, it is annular carbonate preferably.

As these examples of representation, a tetrahydrofuran, 2-methyl tetrahydrofuran, 1,4-dioxane, an anisole, mono-glyme, an acetonitrile, Propionitrile, 4-methyl-2-pentanone, butyronitrile, Valeronitrile, a benzonitrile, 1,2-dichloroethane, gamma-butyrolactone, Dimethoxyethane, a methyl FORU mate, propylene carbonate, Although ethylene carbonate, vinylene carbonate, dimethylformamide, dimethyl sulfoxide, a dimethyl thioformamide, a sulfolane, a 3-methyl-sulfolane, trimethyl phosphate, phosphoric-acid triethyl, these mixed solvents, etc. can be raised It is not necessarily limited to these.

Furthermore, if it requires, a cell is constituted using components, such as a charge collector, a terminal, and an electric insulating plate. Moreover, especially as structure of a cell, although not limited, if it requires further, the gestalt of a positive electrode, a negative electrode, the paper mold cell that used the separator as the monolayer or the double layer when requiring further, a laminating mold cell or a positive electrode, a negative electrode, the cylindrical cell around which the separator was wound in the shape of a roll will be mentioned as an example.

[Effect of the Invention]

It is a small light weight, and the cell of this invention is especially excellent in a cycle property and a self-discharge property, and very useful as power sources the object for small electronic equipment, the object for electric vehicles, for stationary energy storage, etc.

[Example]

Hereafter, an example and the example of a comparison explain this invention in more detail.

Example 1 After mixing 33.3 mol of LiCO(s), and 3042.0 mol of Co(es), it calcinated at 870 degrees C in air for 8 hours, and LiCoO₂ was obtained. It applied to the aluminum foil (15micro) of the back 1cmx5cm angle which made the dimethylformamide solution

(2-% of the weight concentration) 100 weight section of polyvinylidene fluoride distribute the graphite powder of the powder 100 weight section of this LiCoO_2 , and 20 weight sections, and the 125micro positive electrode was obtained at the time of desiccation.

On the other hand, after making the dimethylformamide solution (4-% of the weight concentration) 100 weight section of a polyacrylonitrile distribute the powder 100 weight section of 10micro of mean diameters of needle coke (Koa-SJ-Coke by Koa Oil Co., Ltd.), it applied to the copper foil (10micro) of a 1cmx5cm angle, and the 75micro negative electrode was obtained at the time of desiccation.

The propylene carbonate solution of 1.0M lithium perchlorate was used as the electrolytic solution, the 35micro polyethylene fine porosity film was used as a separator again, and the cell shown in Fig. 1 was assembled.

When it charged by 5mA constant current, open end child electrical-potential-difference 3.95V were shown. It discharged to 1.5V by 5mA constant current after that. It charged by 5mA constant current after this for 1 hour, and the discharge cycle to 1.5V was repeated by 5mA constant current.

The cell engine performance at this time is shown in the 1st table.

Example of reference In the example 1, instead of 3O42.0 mol of Co(es), six mol of NiO(s) were used, it calcinated at 900 degrees C in oxygen for 48 hours, and LiNiO_2 was obtained.

Open end child electrical-potential-difference 3.83V were indicated to be ***** for the cell by the same actuation as an example 1 using this LiNiO_2 at the time.

Example 1 of a comparison It applied to the aluminum foil (15micro) of the back 1cmx5cm angle which made the dimethylformamide solution (2.0-% of the weight concentration) 100 weight section of polyvinylidene fluoride distribute the powder 100 weight section of a banazin san ghost and the powder graphite 20 weight section which have the presentation of V6O13, and the 125micro positive electrode was obtained at the time of desiccation.

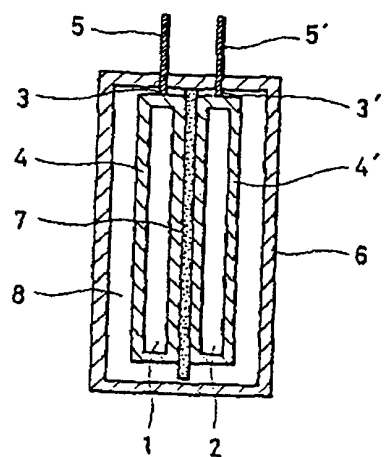
The cell shown in Fig. 1 using the positive electrode which stuck the lithium metallic foil rolled out to the above-mentioned positive electrode was created using the completely same negative electrode as what was created in the example 1.

When cell evaluation was carried out by the same approach as an example 1, open end child electrical-potential-difference 3.20V were shown.

The engine performance of this cell is shown in the 1st table.

第 1 表

	開放端子電圧	1.5Vまでの放電時間	放電容量の変化 (50サイクル/2サイクル)
実施例 1	3.95V	59分	98%
比較例 1	3.20V	21分	66%



- 1---正極
- 2---負極
- 3,3'---集電棒
- 4,4'---SUSネット
- 5,5'---外部電極端子
- 6---電池ケース
- 7---セパレーター
- 8---電解液又は固体電解質